Project ID: mat176

2020 DOE Vehicle Technologies Office Annual Merit Review Presentation

Advanced Anticorrosion Coatings on Lightweight Magnesium Alloys by Atmospheric CO_2 Plasma Treatment*

* Subtask 5A under the Powertrain Materials Core Program (PMCP)

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Project Overview: Advanced Anti-Corrosion Coatings on Mg (Thrust 5, 1-year Exploratory Project)

Timeline/Budget

- Project start: April 2019
- Project end: March 2020
- Percent complete: 100%
- **Subtask 5A Budget**
  - **FY19-20: $157.5K ($150K DOE)**
    - $114K DOE funds to ORNL
    - $43.5k DOE funds to APS
    - Cost share by APS, Inc.: $7.5K

Barriers

- Mg is a low-density metal with very good strength to weight ratio (compared to steel and aluminum), and offers valuable materials light weighting options for future vehicles (up to 50% chasis weight reduction), but has **extremely poor corrosion resistance**
- There are few/no existing large-scale options for affordable, effective corrosion protection of Mg for automotive applications
- Maintenance, Repair and Recycling of Mg alloy components

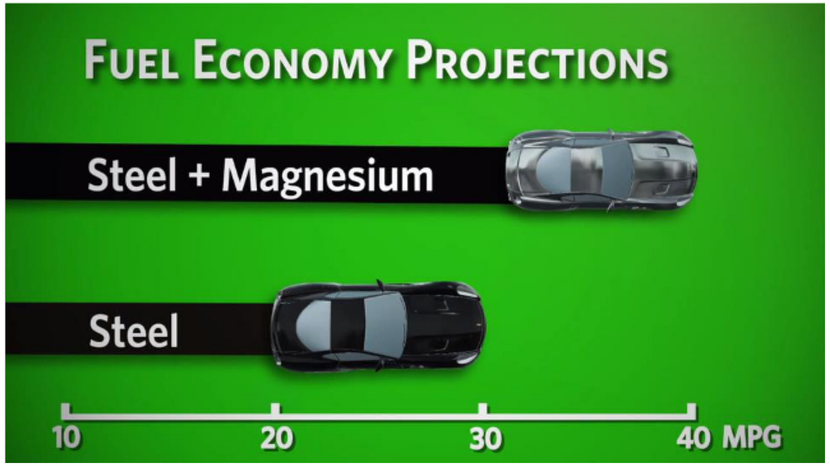
FY20 VTO Powertrain Materials Core Program **Research Thrusts**	FY20 Budget	Participating Labs
Thrust 1. Cost Effective LW High Temp Engine Alloys	$1.05M	ORNL
Thrust 2. Cost Effective Higher Temp Engine Alloys	$1.525M	ORNL, PNNL
Thrust 3. Additive Manufacturing of Powertrain Alloys	$1.075M	ORNL
Thrust 4A. Advanced Characterization & Computation	$1.625M	ORNL, PNNL, ANL
Thrust 5. Exploratory Research(1-year projects) **-Subtask 5A ($150K): Advanced Anti-Corrosion Coatings….** -Subtasks 5B, 5C & 5D ($450K)	$600k	ORNL, PNNL, ANL

Partners

- Project Lead
  - –Oak Ridge National Lab (ORNL)
- Project Partners
  - –**Atmospheric Plasma Solutions (APS), Inc** (Subcontractor & cost share partner)

Relevance – Project Objectives

Impact

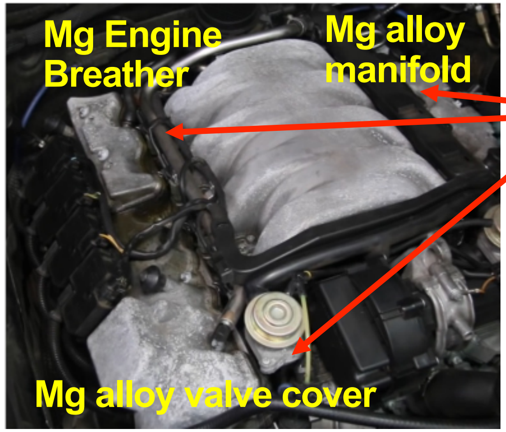


https://insights.globalspec.com/article/7243/magnesium-car-parts-a-far-reach-for-manufacturers-part-1

Objectives

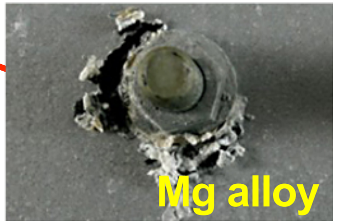
The goal is to develop **an advanced anti-corrosion coating treatment** for light-weight magnesium alloys for powertrain application via **cost-effective atmospheric, room temperature CO_2 chemical plasma techniques**.

Corrosion Issue



Atmospheric Corrosion

https://www.youtube.com/watch?v=dxb0w0_Pw4E "How to Minimize Corrosion on Magnesium Engine Parts: Part 1"



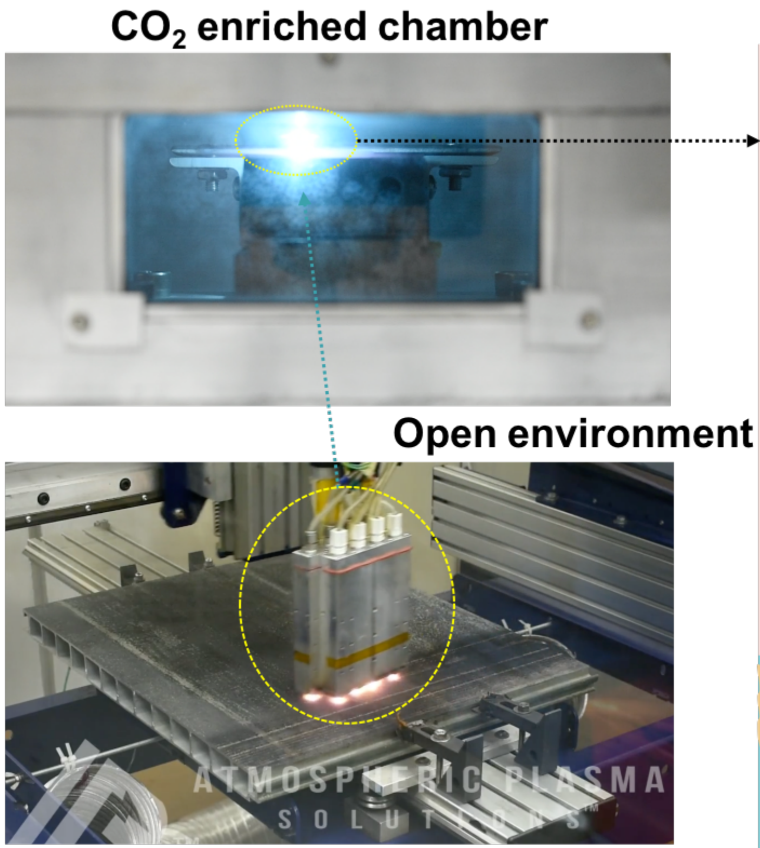
Galvanic Corrosion at Mg/steel Jointing

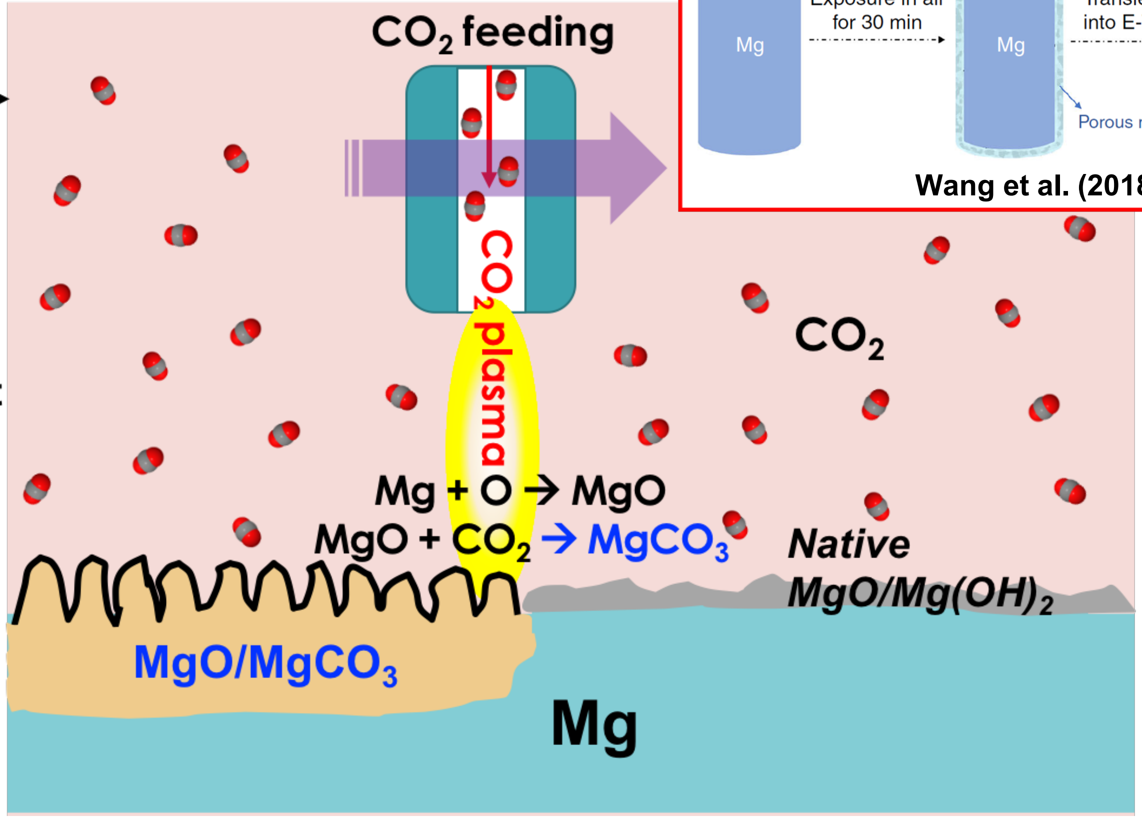
https://www.thefabricator.com/article/metalsmaterials/protecting-magnesium-alloys-from-corrosion

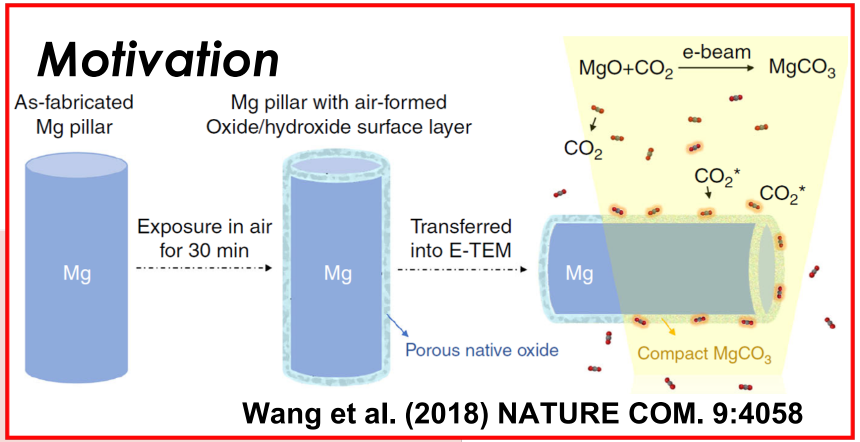
Milestones

1. Demonstrate formation of dense $MgCO_3$ layer
2. Reduction in >10 fold corrosion rate of the new coated Mg/Mg alloy, compared to untreated one

Approach

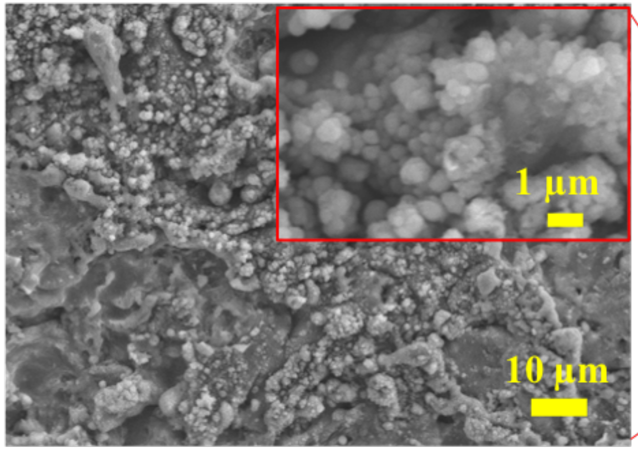


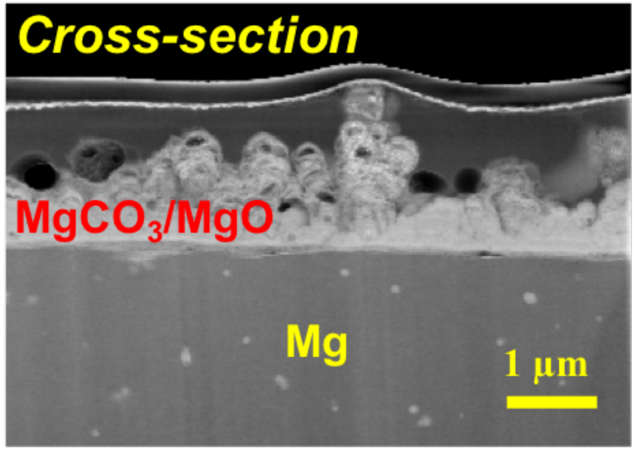


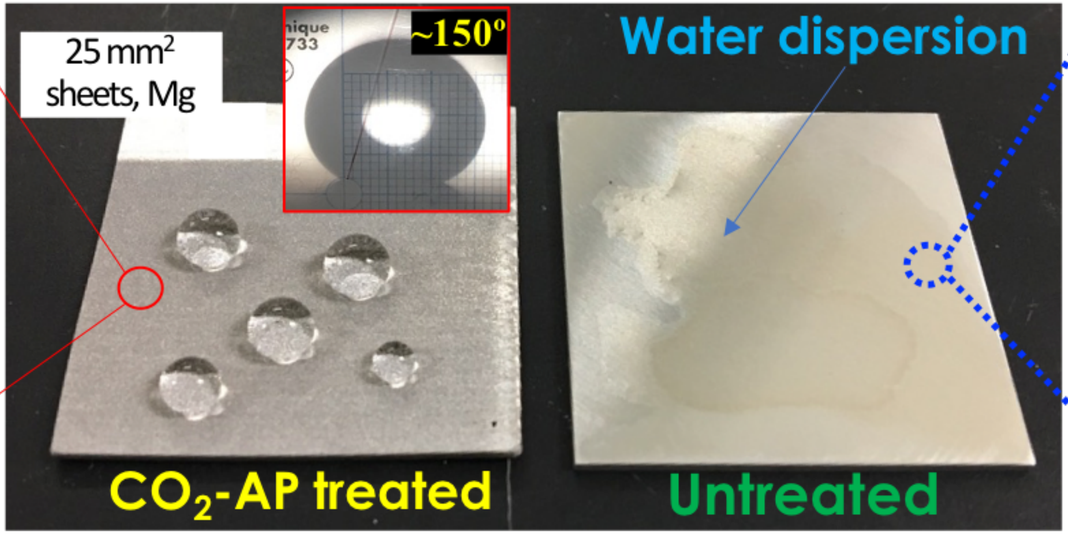


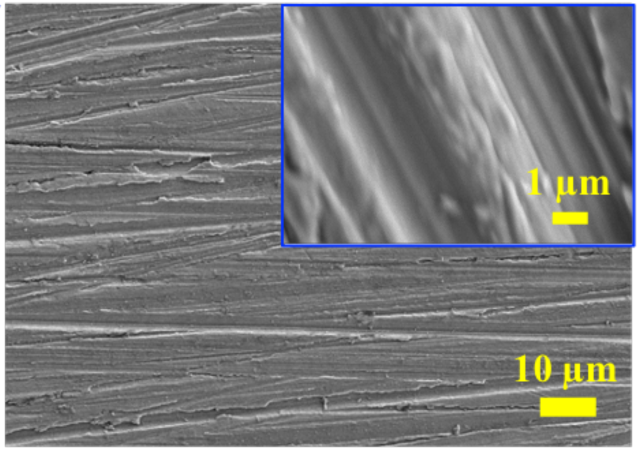
In-line atmospheric CO_2 plasma (CO_2-AP) forms a corrosion protective layer on a Mg alloy surface

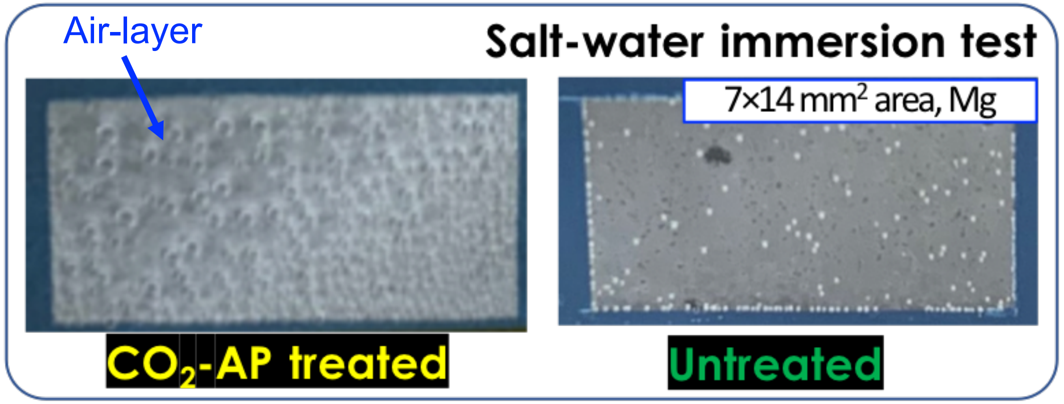
CO_2-AP treatment forms a nano/micro structured surface layer with durable superhydrophobicity.







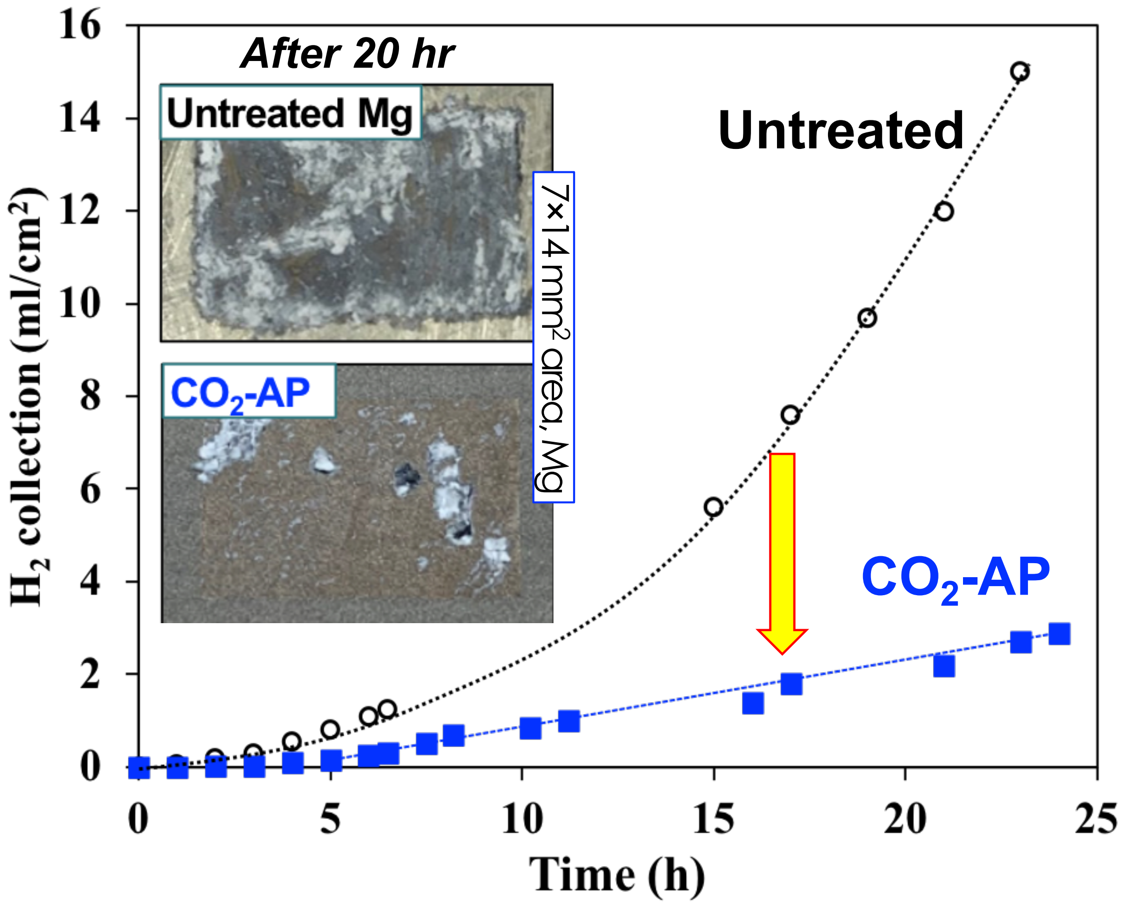




Air-layer on **superhydrophobic** CO_2-AP treated surface under water mitigates salt-water attack

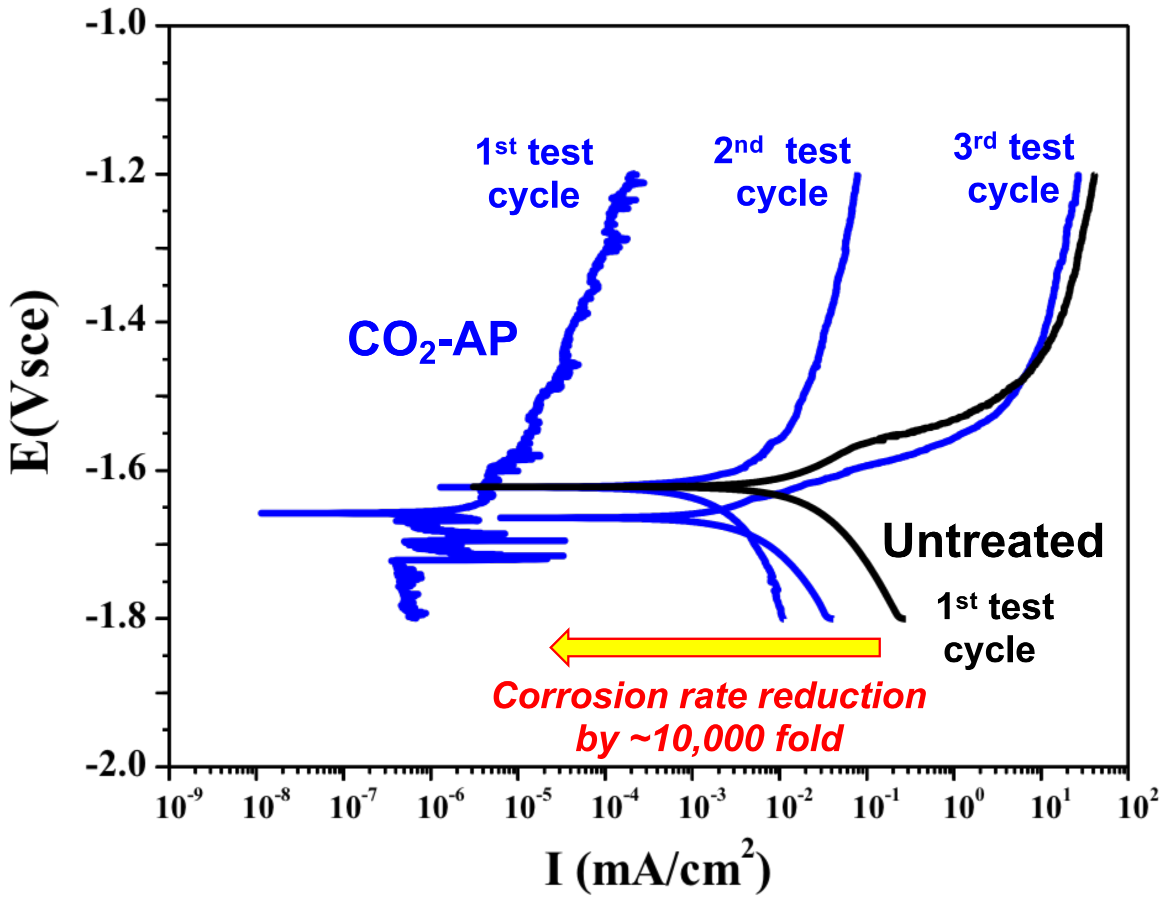
CO_2-AP surface layer provides >10 fold reduction in corrosion rate, compared to untreated Mg

Standard corrosion test: corrosive water immersion



H_2 evolution in 3.5 wt.% NaCl

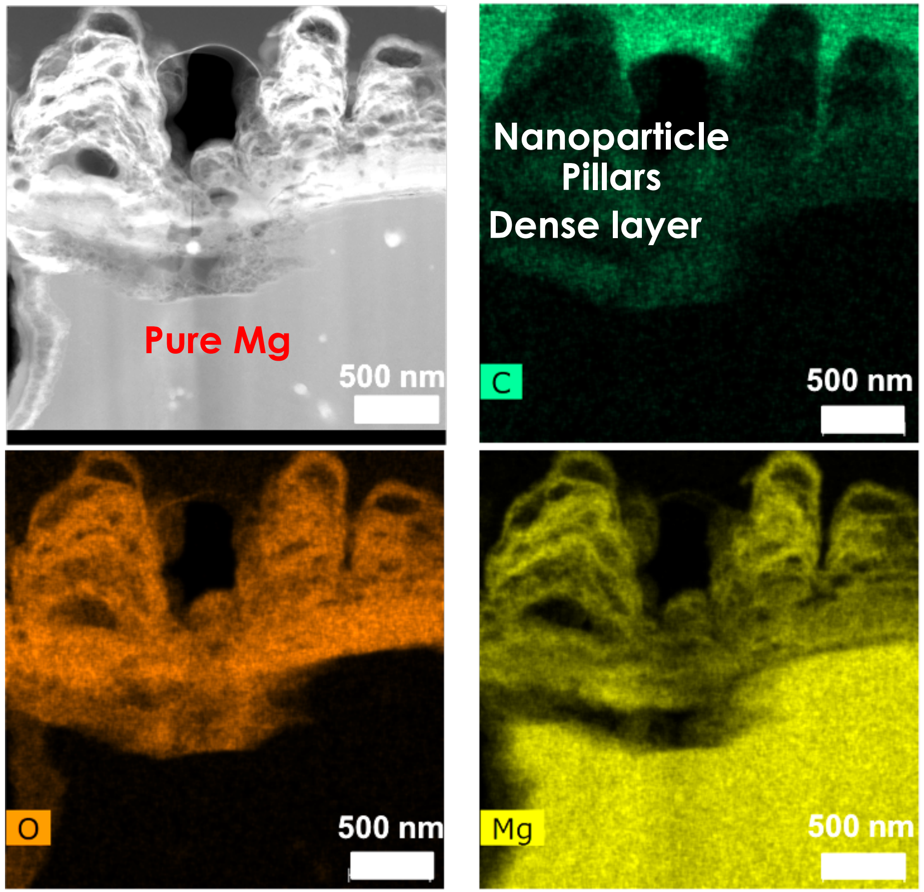
Electrochemical corrosion rate measurement test



Potentiodynamic polarization in 3.5 wt%. NaCl

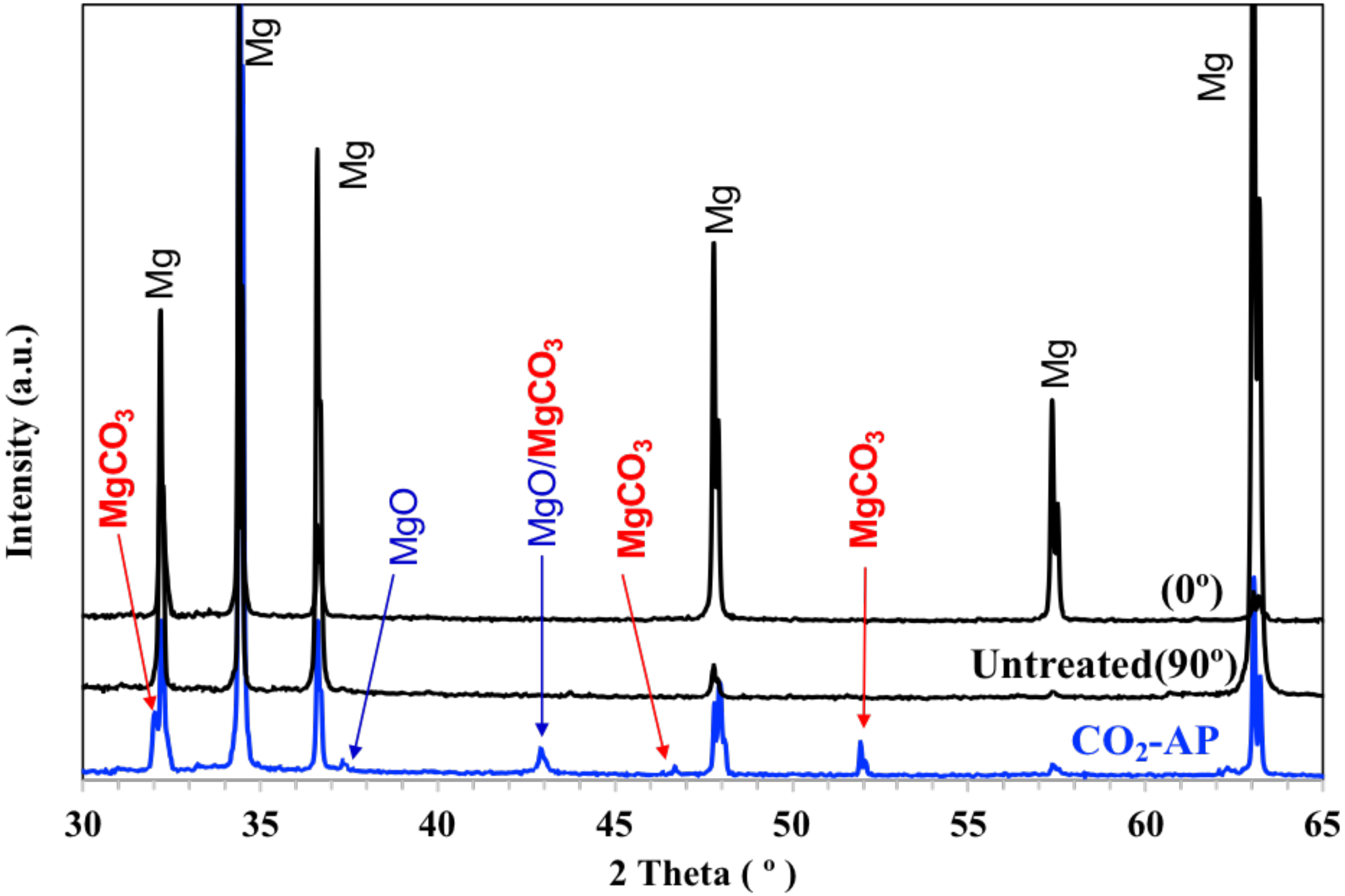
CO_2-AP surface layer contains Carbonate/$MgCO_3$/MgO

Cross-sectional CO_2-AP layer on Mg



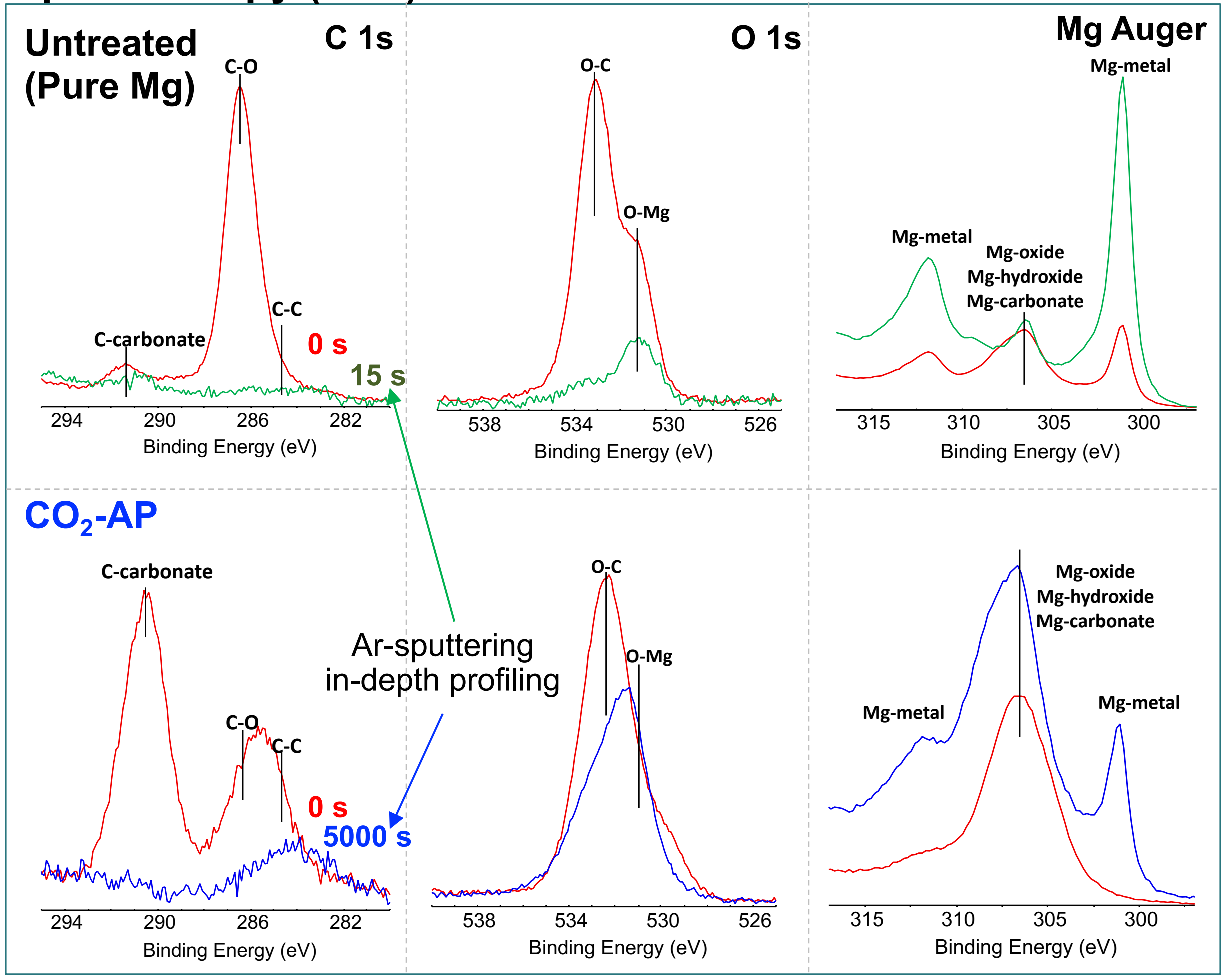
High angle annular dark field (HAADF)-STEM with EDX elemental mapping

X-ray diffraction study on CO_2-AP layer



Technical Accomplishment

Surface characterization by X-ray photoelectron spectroscopy (XPS)

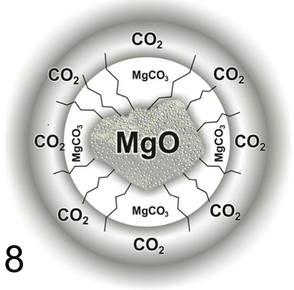


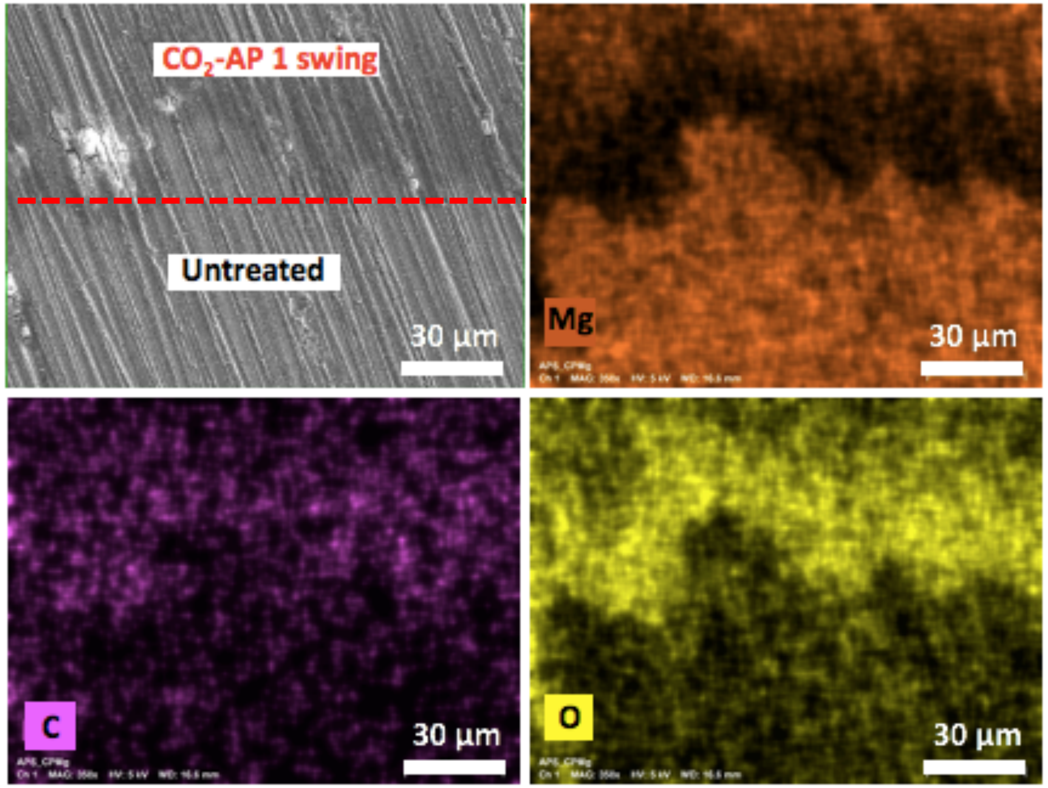
"MgO adsorbs CO_2"

Theoretical CO_2 uptake capacity

: **1.09 g of CO_2 per gram** of sorbent

Energy Environ. Sci. 2014, 7, 3478-3518



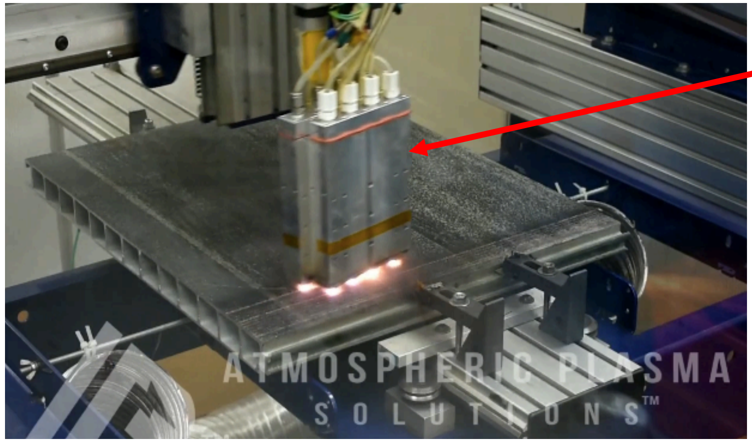


SEM with Energy dispersive X-ray spectroscopy (EDX)

XPS and SEM-EDX shows carbonate layer formation on CO_2-AP treated area

OAK RIDGE National Laboratory

Collaboration and Coordination with Other Institutions



8 beams array of Atmospheric Plasma Solution (APS)

ATMOSPHERIC PLASMA SOLUTIONS™

APS treated magnesium specimens (e.g., pure commercial magnesium and AZ31B) under different CO_2 plasma operation conditions and transfer the treated specimens to ORNL for evaluation.

Proposed Future Research

- Depending on Mg alloy types with different thermal-mechanical properties and reactivity, each operational condition and pretreatments must be studied to ensure the effective protection.
- CO_2- AP process needs to evaluate the coating feasibility in a multi-layer coating protection scheme for practical application

Any proposed future work is subject to change based on funding levels.

Summary

- This 1-year exploratory project successfully completed and achieved all milestones.
- The scalable CO_2-AP treatment demonstrated the formation of a potentially effective anti-corrosive layer that is associated with the nano/micro structured conversion ($MgO/MgCO_3$) layer and its superhydrophobic surface features.
- New Findings:
  - Chemically active CO_2 plasma ablates a portion of Mg surface & forms $MgO/MgCO_3$ intermixed nanoparticle layer on the plasma converted surface
  - The active CO_2 molecules simultaneously bind on the MgO surface to form carbonate layers, resulting in a superhydrophobic surface.

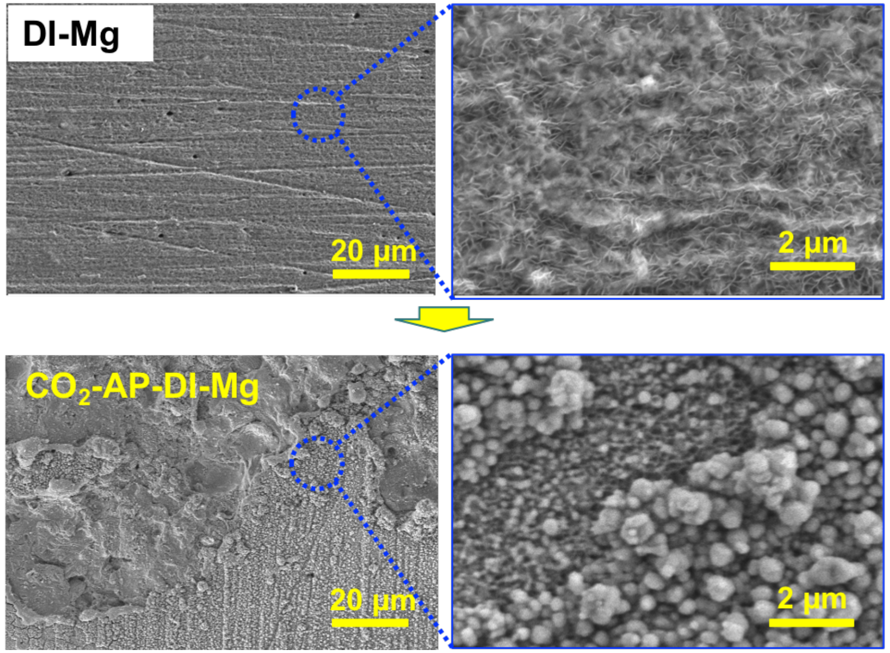
Back up slides

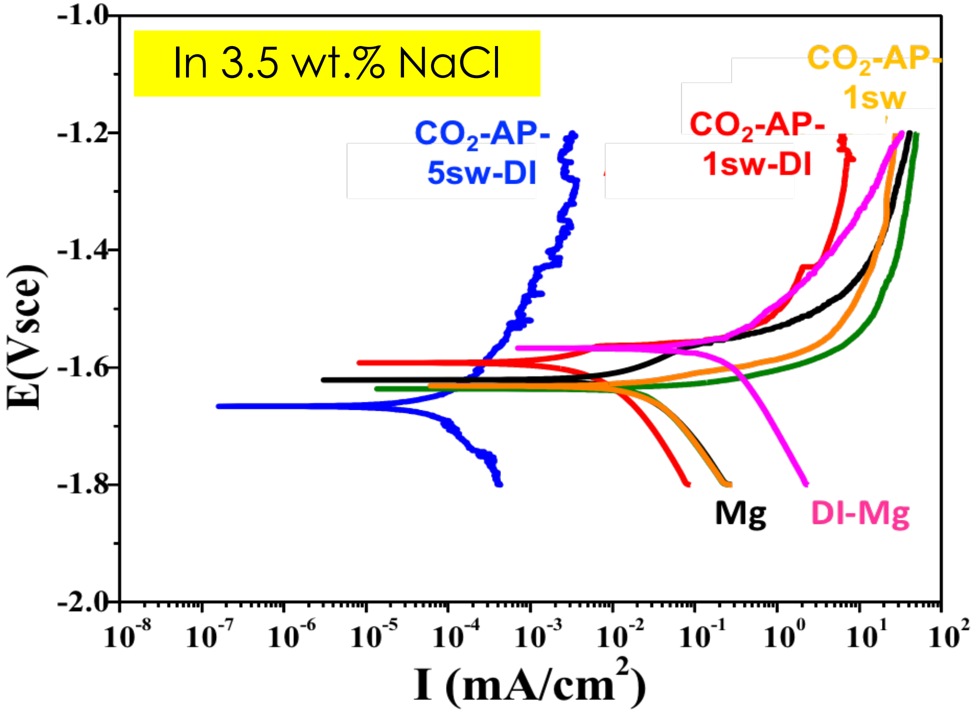
Proposed Future Research

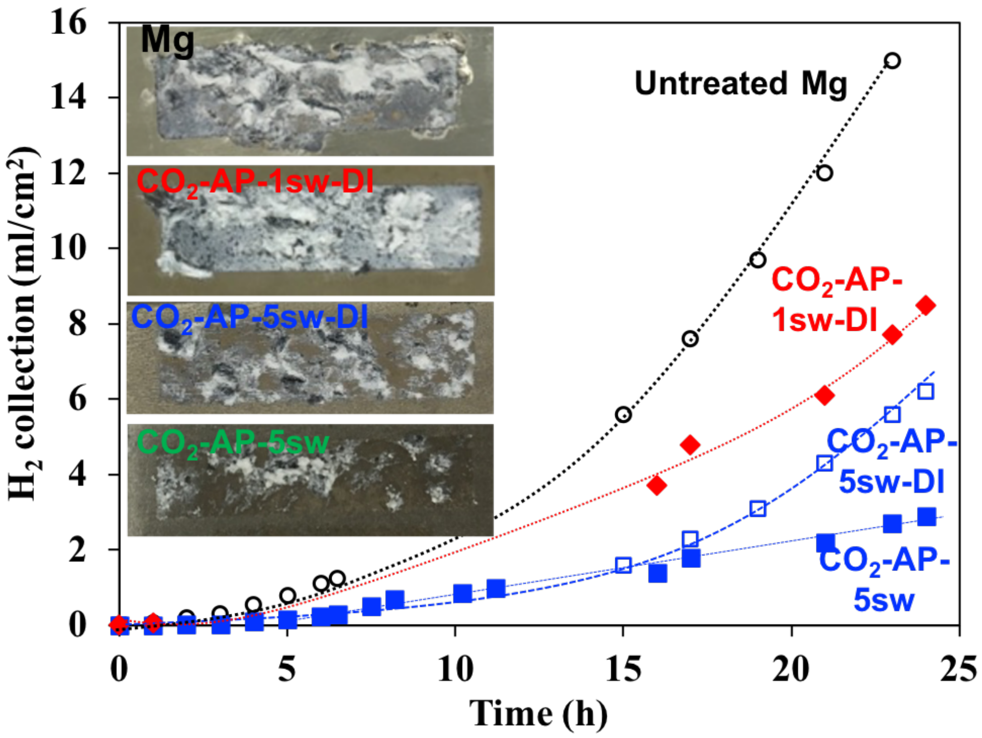
- This is a one year exploratory project=no future work

Any proposed future work is subject to change based on funding levels.

Technical Back-up slides

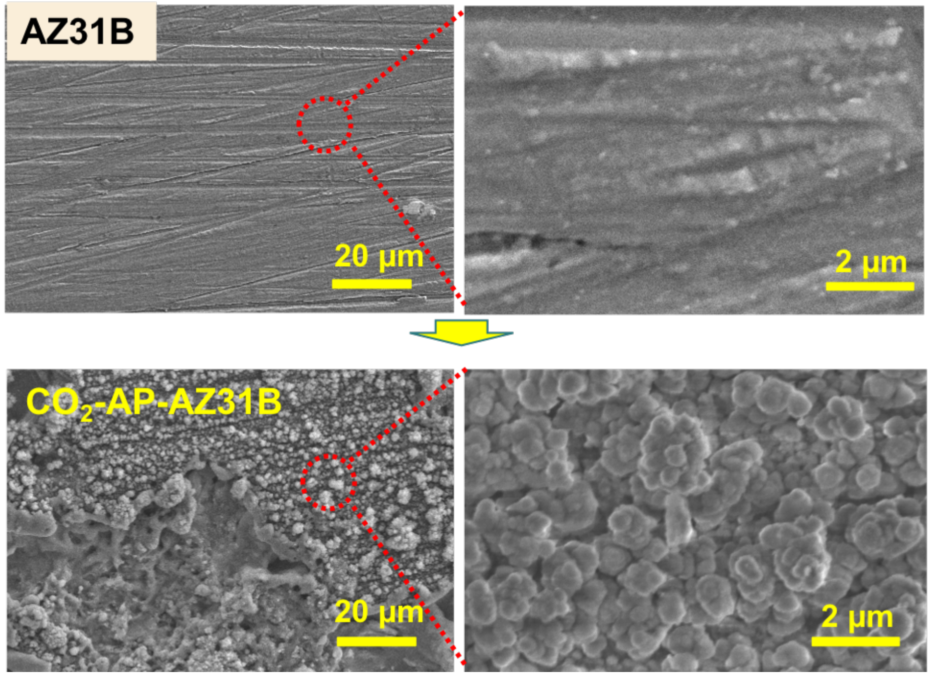


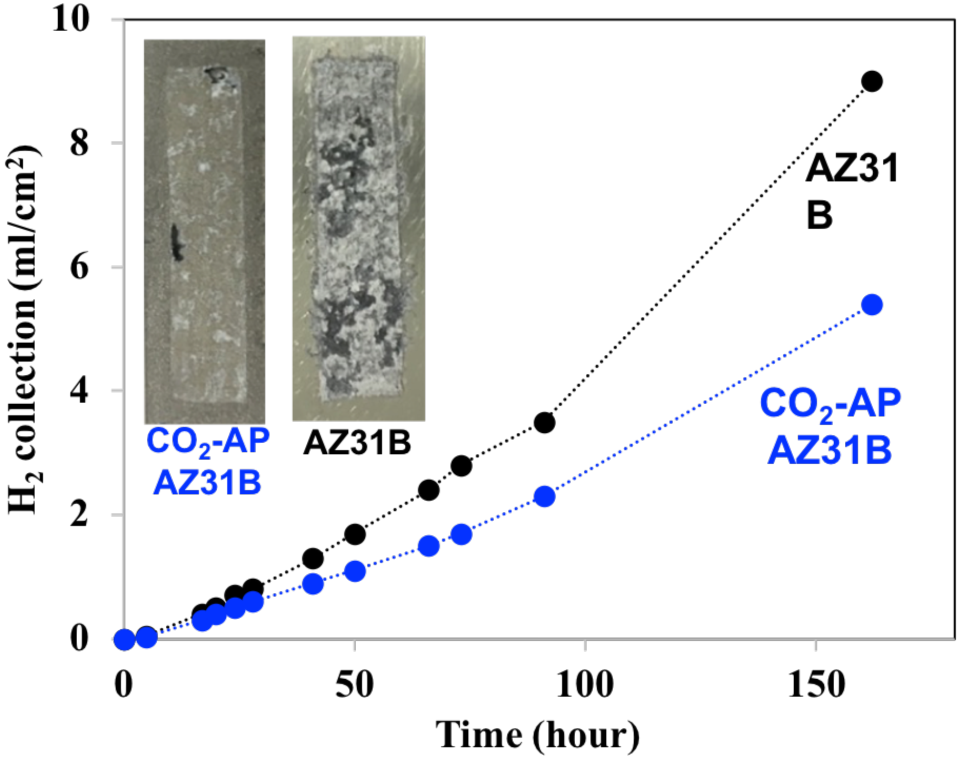


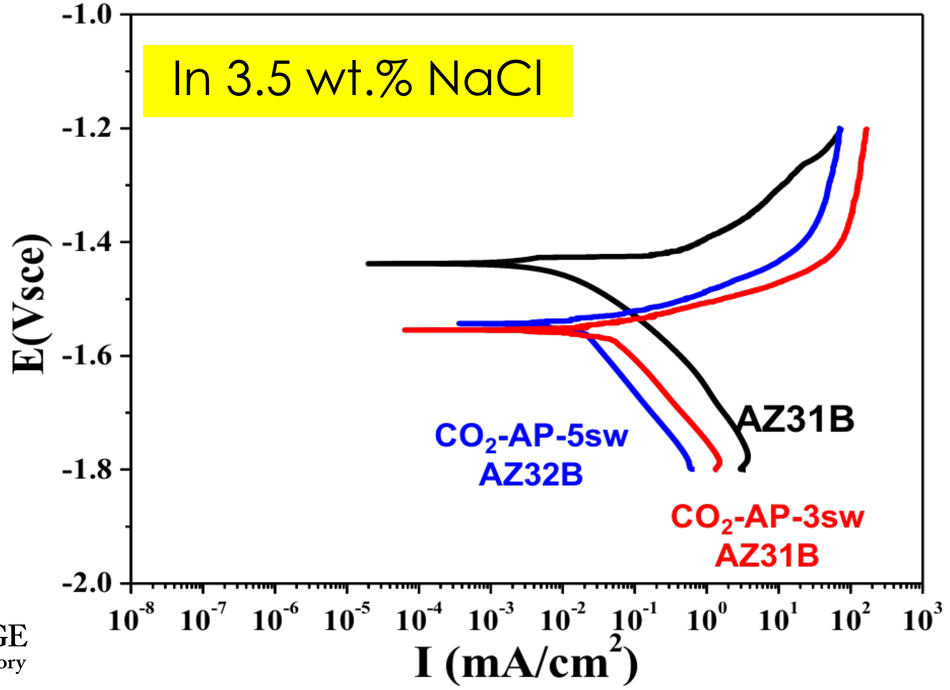


"CO_2 AP treatment on deionized water pretreated Mg samples (MgO) shows anti-corrosion effect"

Technical Back-up slides







"CO_2 AP treatment on Mg alloy (AZ-31B) samples shows minor anti-corrosion effect. Further study is necessary"

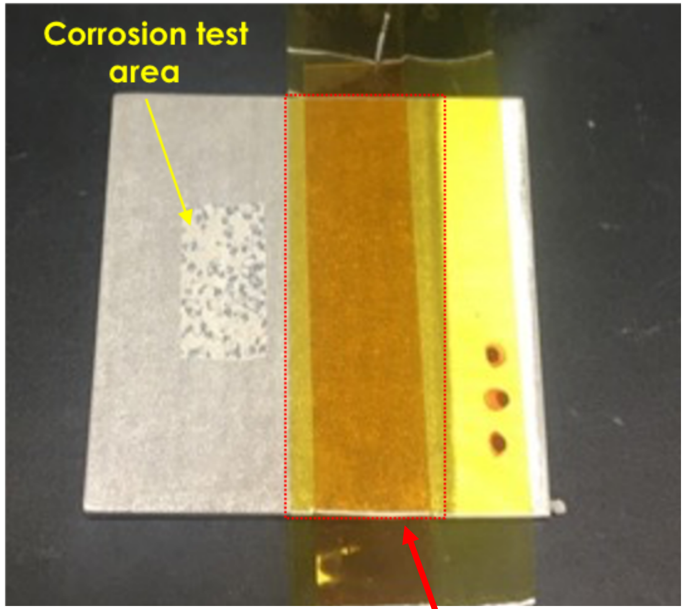
Comparison of corrosion resistance: CO_2-AP treated surface

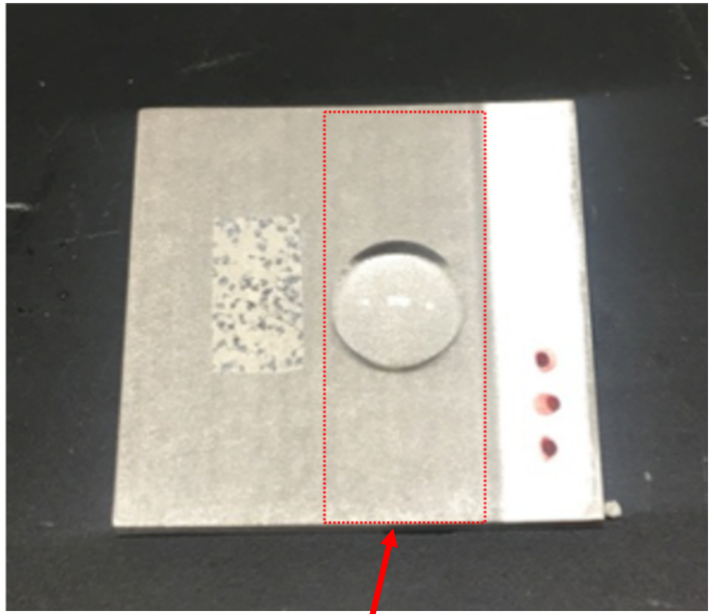
Sample	Zero Current Potential (V_{sce})	i_{corr} ($\mu A/cm^2$)
Mg	-1.62	**28.55**
DI water pretreated Mg	-1.56	**243.9**
CO_2-AP-1sw	-1.62	**30.67**
CO_2-AP-1sw-DI	-1.59	**6.64**
CO_2-AP-5sw-DI	-1.66	**0.058**
CO_2-AP-5sw (1/2/3 test cycles)	-1.66/-1.62/-1.66	**0.00222/2.09/6.02**
Mg[1]	-1.58	196.6
DI water pretreated Mg[1]	-1.59	251.3
CO_2 arc Plasma[1]	-0.73	0.22
Anodizing coating[2]	-1.48	27
Composite coating by micro arc oxidation[3]	-1.49	0.69
Micro-arc oxidation coating[4]	-1.69	0.17

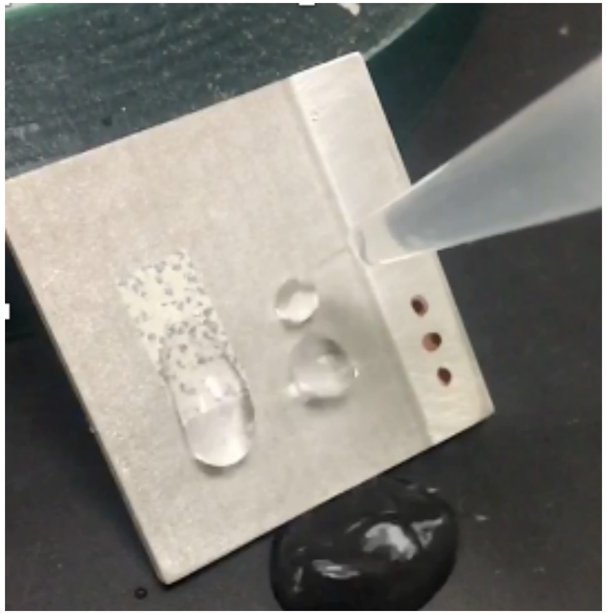
Our study

*Determined by extrapolated cathodic current and corrosion potential (Ecorr)
* sw: plasma sweep number

1. Wang et al Turning a native or corroded Mg alloy surface into an anti-corrosion coating in excited CO2. Nature Communications 9, 4058 (2018)
2.Xue, D., Yun, Y., Schulz, M. J. & Shanov, V. Corrosion protection of biodegradable magnesium implants using anodization. *Mater. Sci. Eng. C* **31**, 215-223 (2011).
3.Mu, W. & Han, Y. Characterization and properties of the MgF_2/ZrO_2 composite coatings on magnesium prepared by micro-arc oxidation. *Surf. Coat. Tech.* **202**, 4278-4284 (2008).
4.Zhao, L., Cui, C., Wang, Q. & Bu, S. Growth characteristics and corrosion resistance of micro-arc oxidation coating on pure magnesium for biomedical applications. *Corros. Sci.* **52**, 2228-2234 (2010).







Taping test on untested area

“CO_2 AP treatment on Mg samples forms durable superhydrophobic coating”